Development of Venturi/Vortex Scrubber Technology for Controlling Chromium Electroplating Hazardous Air Emissions

by
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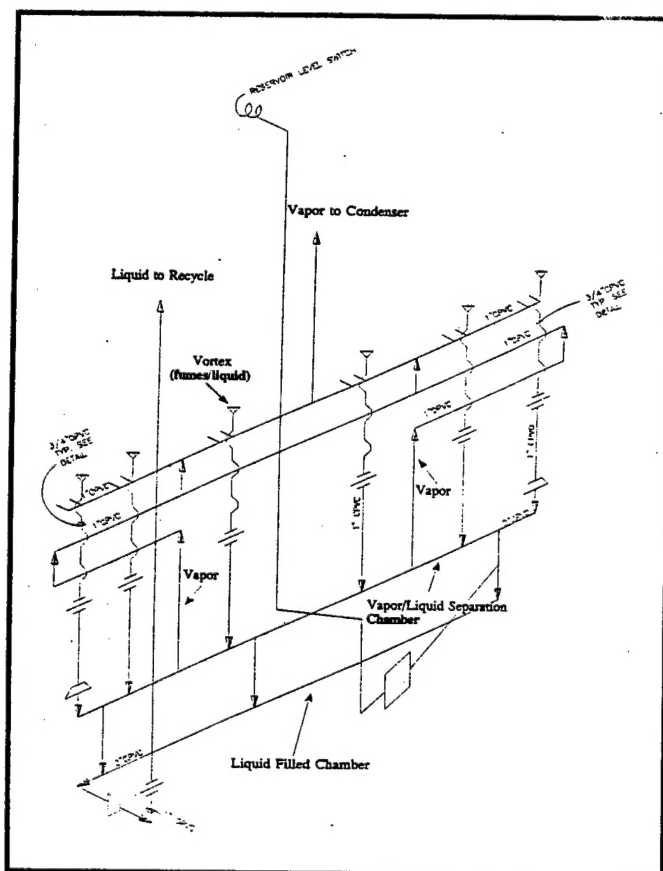
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Chromium has a combination of qualities that give chromium electroplating an important role in coating military hardware and armament. However, chromium electroplating and chromium anodizing operations create hazardous air pollutants in the form of hexavalent chromium. Conventional technologies for controlling this pollutant are expensive, noisy, and use a lot of energy and water. Consequently, an air pollution problem is turned into a water pollution problem that also requires treatment. There is a need for an economical control option that pollutes less than conventional technologies. This project developed control technologies to effectively and economically control hazardous air emissions from Army chromium electroplating and anodizing operations, primarily focusing on the development of the Venturi/Vortex Scrubber technology (VVST).

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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit U05, "Abatement of Hazardous Air Pollutant Emissions From Plating Operations." The technical monitor was Louis Kanaras, SFIM-AEC-EPD.

The work was performed by the Industrial Operations Division (UL-I) of the Utilities and Industrial Operations Laboratory (UL), U.S. Army Construction Engineering Research Laboratories (USACERL). The USACERL principal investigator was Dr. K. James Hay. Walter J. Mikucki is Chief, CECER-UL-T; Martin J. Savoie is Acting Operations Chief, CECER-UL; and Gary W. Schanche is the responsible Technical Director, CECER-UL. The USACERL technical editor was William J. Wolfe, Technical Resources.

COL James A. Walter is Commander and Dr. Michael J. O'Connor is Director of USACERL.

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1 Introduction

Background

Chromium has a combination of qualities that are very difficult to substitute: hardness, high reflectance, high corrosion resistance, low coefficient of friction, high heat conductivity, and excellent wear resistance. Together, these properties give chromium electroplating an important role in coating military hardware and armament. Unfortunately, chromium electroplating and chromium anodizing operations create hazardous air pollutants in the form of hexavalent chromium. Hexavalent chromium has known carcinogenic properties and is highly regulated by the U.S. Environmental Protection Agency (USEPA), the Occupational Safety and Health Administration (OSHA), and State regulatory agencies (Federal Register, vol 60, Code of Federal Regulations [CFR] 29:1910).

The USEPA has promulgated a National Emission Standard for Hazardous Air Pollutants (NESHAP), which regulates the chromium air emissions generated from chromium electroplating and anodizing operations (60 FR 4948). The final rule, published 25 January 1995, sets a compliance deadline of 25 January 1997. Under this rule, a chromium electroplating or anodizing facility may select the means to reduce emissions as long as compliance is demonstrated. State regulatory agencies may enforce stricter regulations.

The inefficiency of the chromium electroplating process creates byproduct gases that rise to the plating surface and burst, creating a mist of chromic acid above the electroplating tanks. Conventional technologies for controlling this pollutant are end-of-pipe control devices such as packed bed scrubbers and composite mesh pad units. These devices are expensive, noisy, and use a lot of energy and water. Consequently, an air pollution problem is turned into a water pollution problem that also requires treatment. There is an opportunity and a need for an economical control option that pollutes less than conventional technologies.

Objectives

The objective of this project was to develop control technologies that effectively and economically control hazardous air emissions from Army chromium electroplating and anodizing operations. This study primarily focused on the development of the Venturi/Vortex Scrubber Technology (VVST).

Approach

This work is a continuation of the research reported in U.S. Army Construction Engineering Research Laboratories (USACERL) Interim Report *Abatement of Hazardous Air Pollutant Emissions From Army Chromium Electroplating and Anodizing Operations* (Hay 1996), which introduced the Venturi/Vortex Scrubber Technology for this application. Development consisted of four stages:

1. The original bench scale experiment not conducted by USACERL

2. The USACERL pilot demonstration at Benet Laboratory, New York (prototype 1)

3. The testing of prototype 2 at USACERL

4. The development of prototype 3 at USACERL.

This technology has been developed specifically for controlling/recycling chromium electroplating emissions and is intended to replace conventional emission technologies.

Scope

This study investigated the development of the venturi/vortex scrubber technology up until the demonstration stage. Information regarding current DOD operations is current as of 24 January 1997.

Mode of Technology Transfer

The control technology to effectively and economically control hazardous air emissions from chromium electroplating and anodizing operations developed as part of this research will be transferred to the Army industrial user community, and other military and private sector operations where the technology is

applicable. It has been selected to be demonstrated and validated as part of the Department of Defense (DOD) Environmental Security Technology Certification Program (ESTCP). Two demonstrations will take place, one at Marine Corps Logistics Base in Albany, GA, and the other at Hill Air Force Base, UT. A technology transfer plan will be developed and executed as part of that project.

Metric Conversion Factors

The following metric conversion factors are provided for standard units of measure used throughout this report:

1 in.	=	25.4 mm
1 ft	=	0.305 m
1 cu ft	=	0.028 m^3
1 gal	=	3.78 L
1 °F	=	(°C x 1.8) +32
1 psi	=	6.89 kPa

2 Chromium Electroplating and DOD Operations

Technical Overview

Hard Chromium Electroplating

The chromium electroplating process is widely used for depositing chromium metal onto a substrate, typically steel, for hard chromium electroplating. In the chromium electroplating process, a direct current is applied between the anode(s) and cathode(s) (of the part) while it is suspended in a hexavalent chromium (chromium in the +6 valence state) plating solution.   The bath temperature is usually kept between 50 and 65 °C. The bath contains 225 to 375 g/L (usually 240 g/L) of chromic anhydride (CrO_3), creating an aqueous solution of chromic acid (H_2CrO_4). Sulfuric acid (H_2SO_4) is also present at 2.25 to 3.75 g/L to act as a bath catalyst. At these high concentrations, the chromic acid forms dichromic acid ($H_2Cr_2O_7$) which then ionizes to dichromate ($Cr_2O_7^{-2}$) and hydrogen (H^+) ions.

Three chemical reactions occur at the cathode (part):   the deposition of chromium on the part surface, the evolution of hydrogen gas (H_2), and the reduction of hexavalent chromium to trivalent chromium (+3 valence state). Three reactions also take place at the anode, which is usually made of lead alloyed with tin or antimony: the oxidation of the anode, the evolution of oxygen gas (O_2), and the oxidation of trivalent chromium to hexavalent chromium. The surface area of the anode is necessarily larger than the surface area of the part to be plated to ensure that this last reaction takes place. This helps minimize the contamination of the bath by trivalent chromium.

Chromium electroplating is a very inefficient process in that over 80 percent of the applied energy goes into the evolution of the byproduct gases (hydrogen and oxygen). This inefficiency of the electroplating process is the contributing factor to the creation of emissions (USEPA July 1993).

Chromium Anodizing

Chromium anodizing is the process of electrolytically oxidizing the surface of a substrate, typically aluminum. An oxidized layer on the surface of a part provides corrosion resistance, low conductivity, and an accepting surface for coloring. Although there are different types of anodizing processes, chromium anodizing offers the advantage that chromic acid acts as a corrosion inhibitor while remaining in the pores and crevices of a part (USEPA July 1993). This advantage makes chromium anodizing a preferred method for anodizing military aircraft parts.

The equipment used for chromium anodizing and chromium electroplating are very similar with the exception that with anodizing, the part is the anode and the tank is the cathode. The process differs from electroplating in that the voltage is varied during an anodizing operation, and the chromic acid concentration and bath temperature are lower.

Creation of Emissions

The oxygen and hydrogen gases that are generated at the cathode and anode during the electroplating or anodizing process rise to the plating bath surface as bubbles, then escape as the bubbles burst. Each bursting bubble ejects a small drop of plating solution into the air above. The cumulative effect is a fine mist above the plating tank. The amount of gases generated is a function of the electrochemical activity in the tank, controlled by the bath composition, bath temperature, current applied, and the surface area of the part(s). Emissions will be a direct function of the generation of gases, but can be affected by the surface tension of the plating solution, shape of the part(s), depth and arrangement of the part(s) and anode(s), and any physical barrier located at the solution/air interface. The USEPA (July 1993) found an average emission generation for hard chromium electroplating operations of 10 mg/ampere-hour (amp-hr) with a range of values from 3.2 to 22.5 mg/amp-hr.

In an anodizing operation, emissions are generated in the same manner as for hard chromium electroplating with the exception that emissions will decrease with anodizing duration. As an oxide layer grows on the part, the resistance to current increases, thereby decreasing the generation of gases and emissions.

Miles, Miles, and Michel (1995) reported that particulate emissions from a hard chromium electroplating facility were in the size range of 0.3 to 25 μm in diameter with the mean diameter near 8 μm (Powers 1985). These small aerosol

particles of plating solution can become even smaller through evaporation as they are exposed to ambient air.

DOD Operations

Hay (1996) presented a table listing Army facilities with chromium electroplating and/or anodizing operations. Since that report, Stratford Army Engine Plant has ceased operation of their chromium anodizing tank and Crane Army Ammunition Plant has been identified as possibly possessing chromium electroplating tanks. In addition to the eight Army installations, there are eight Navy, and five Air Force facilities:

Army

- Rock Island Arsenal
- Watervliet Arsenal
- Corpus Christi Army Depot
- Red River Army Depot
- Anniston Army Depot
- Lake City Army Ammunition Plant
- Letterkenny Army Depot
- Crane Army Ammunition Plant

Navy

- Cherry Point Naval Aviation Depot
- North Island Naval Aviation Depot
- Puget Sound Naval Shipyard
- Louisville Naval Ordnance Station
- Marine Corps Logistic Base Albany
- Jacksonville Naval Aviation Depot
- Norfolk Naval Shipyard
- Kings Bay Naval Submarine Base

Air Force

- Hill Air Force Base
- Robins Air Force Base
- Tinker Air Force Base
- Kelly Air Force Base
- McClellan Air Force Base.

Regulatory Issues

NESHAP

As part of the Clean Air Act Amendments (CAAA) of 1990 (42 USC 7412), the USEPA was required to establish National Emission Standards for all major sources and some area sources for 189 hazardous air pollutants (HAP). Due to the documented carcinogenic nature of hexavalent chromium (50 FR 24317), the USEPA targeted the electroplating industry as a major source of hexavalent chromium air pollution (57 FR 31576) and proceeded to create regulations pertaining to this industry. The NESHAP for chromium electroplating and anodizing, first proposed on 16 December 1993 (58 FR 65768), was published in the Federal Register on 25 January 1995 (60 FR 4948).

This NESHAP imposes chromium emission concentration limits and/or plating bath surface tension limits for chromium electroplating and anodizing major and area sources, where a source has been defined as one electroplating or anodizing tank. Hard chromium electroplating and anodizing sources must be in compliance by 25 January 1997. The chromium emission concentration limit is 0.015 mg/dscm for large facilities, and 0.030 mg/dscm for small facilities. The cutoff between large and small facilities is 60 million ampere-year (amp-yr) of usage. In general, a DOD facility with more than two tanks will be classified as large. Anodizing facilities can opt for the surface tension limit of 45 dynes/cm. Note that the measured exhaust concentration of chromium can be either a hexavalent chromium concentration or a total chromium concentration; the choice is made by the facility.

The NESHAP is based on output concentration (mg Cr/dscm) from the Maximum Achievable Control Technology (MACT) as opposed to usage (mg Cr/amp-hr). This is due to an assumption derived from data compiled in the rulemaking process that the output concentration of modern control devices (or MACT) is independent of input concentration (USEPA July 1993b). This is a potential concern for the venturi/vortex technology. This device processes a low air flow rate. The total mass rate of released chromium will be less than MACT, but the concentration may be higher. The USEPA will need to grant an alternative technology exception for a facility to use this technology for compliance.

State Regulations

The USEPA has given the States the option to either adopt the Federal regulation (60 FR 4948) or to create/modify State regulations that are at least as stringent. Every State that is relevant to the Army's chromium electroplating and anodizing operations will adopt or has adopted the Federal regulation along with some type of ambient air level or risk-based standard addition as part of their permitting process. An ambient air level standard usually refers to a maximum allowable hexavalent chromium concentration at the fenceline of the facility over a certain time-weighted average. Risk-based standards refer to a health risk to an individual; usually a maximum concentration beyond the fenceline is considered. The USEPA, as required under the CAAA, will also consider risk-based standards as well as part of the next stage in regulations scheduled to occur about 7 years after the final rule was published. Some States plan to wait until this happens before modifying their own regulations. Regulations for States with Army chromium electroplating and/or anodizing operations and their considerations are presented in Hay (1996).

OSHA Requirements

The current OSHA worker breather zone chromium concentration limit or TLV is set at 0.05 mg/m^3 (29 CFR 1910.94). This requirement was scheduled to change near the end of the 1995 calendar year with an expected value of 0.5 μg/m^3 as an 8-hour time weighted average. Altmeyer (1996) noted that the regulation was never changed and future regulatory plans are unknown.

3 Background on VVST

The venturi/vortex scrubber or CH system is a device that pulls chromium-laden air above the plating tank down drains along with the plating solution, thereby recycling the chromium emissions (Castle 1992). Castle had the unit tested (in 1991) and collected favorable results. In the Army, the potential of this technology was first recognized by Philip Darcy of Watervliet Arsenal, who conveyed the information to the principal investigator at USACERL for consideration in this project.

Basic Process Description

Figure 1 shows a basic diagram of the CH system. The unit consists of two primary components: the venturi/vortex scrubber and the filter-condenser assembly. The venturi/vortex scrubber consists of one or more drains with a cone-shaped funnel placed near the surface of the plating solution. Plating solution is drawn down the drains by gravity, creating a vortex. Air above the solution is pulled down the drain and mixed with the solution by flowing through several curved sections in the drain tube. Most of the particulates contact the plating solution and are recycled during this mixing stage. The gas/liquid mixture then flows into a separation vessel. From the separation vessel, the liquid is pumped back into the plating tank and the gases are purged through the filter-condenser. The filter-condenser unit is loosely packed with polypropylene fiber-fill to collect the remaining particulates. The condensate is collected to be recycled and the gases are vented to the atmosphere.

Conventional air circulation promotes emission generation by contributing additional bubbles. This device has a number of advantages over conventional end-of-pipe technologies. The system:

- uses no extensive ventilation system

- costs about 70 percent less

- uses far less energy than conventional technologies

- makes less noise than conventional technologies

- creates no wastewater

- recycles chromium emissions

- eliminates air tank circulation.

The device can be easily modified to accommodate most electroplating tanks. Almost the entire system is constructed of chlorinated polyvinyl chloride (CPVC).

It is recommended that a tank lid be used with this system. The low gas flow rates are not sufficient to prevent all fugitive emissions, especially where there are large air disturbances near the tank. The lid needs to be loose fitting to allow for replacement air from outside the tank lid to be drawn into the system.

Initial Bench Testing

A bench-scale evaluation of the CH system was performed by the Bay Area Air Quality Management District of California in 1991 at the request of Castle Hone and Lap. A single drain unit was placed on a 15.5-gal tank with 100 DC amp of
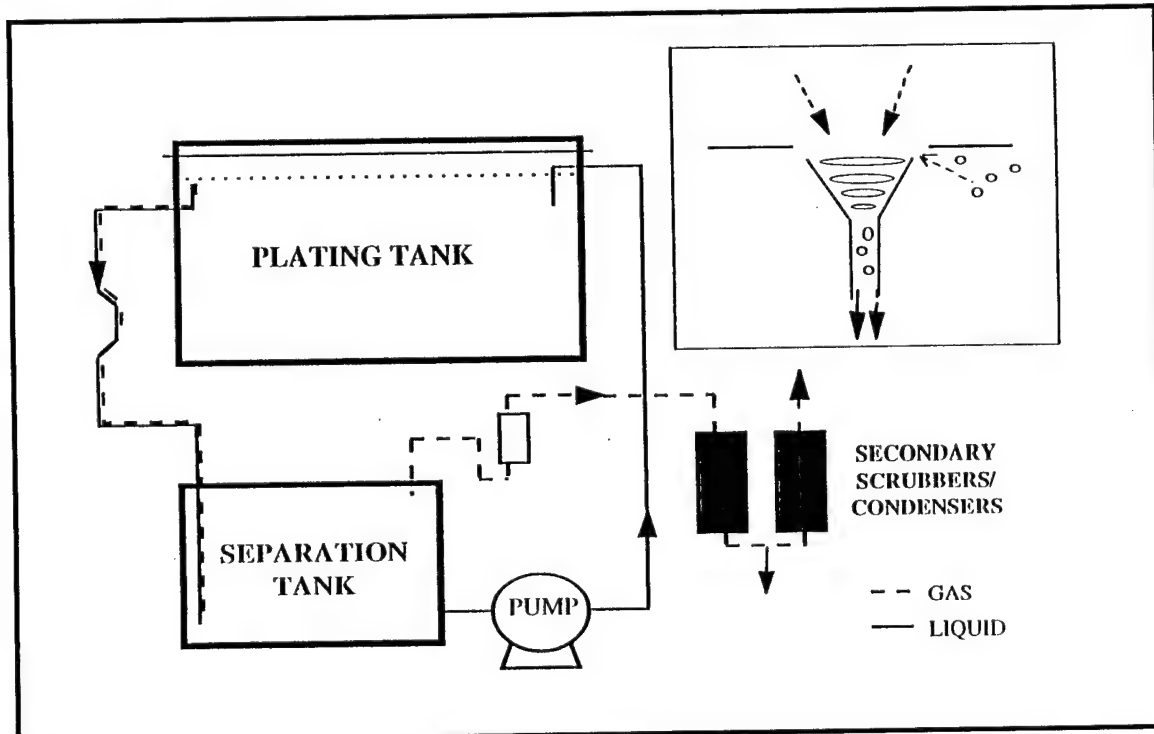
Figure 1. Basic diagram of Castle Hone system.

applied current at 5 volts. Sampling was conducted at two points: immediately upstream and downstream from the filter-condenser assembly of the CH system. Chromium sampling was performed using the California Air Resources Board Method 425 with considerable modifications. The most significant modification is that the chromium fumes were allowed to collect passively in the downstream sampling impingers rather than being drawn in with a pump as specified by approved USEPA sampling methods. This approach was necessary because the exiting gas line was small enough so that the entire gas effluent was sampled. The chromium concentration was measured upstream as 19.2 mg/m^3 (0.014 mg/amp-hr) and downstream as 0.023 mg/m^3 (0.0000156 mg/amp-hr).

The gas volume flow rate was measured using method ST-17. The upstream gas flow rate measurement was 2.5 standard dry cubic feet per hour (sdcfh) at 128 °F and 5.8 percent volume water. The downstream gas flow rate measurement was 2.4 sdcfh at 77 °F and 3.4 percent volume water.

The results of the sampling showed that the system is able to reduce the emissions below the strict California standard of 0.006 mg/amp-hr. There is a large emission reduction across the filter/condenser portion of the device. However, the amount of reduction accomplished by the venturi/vortex scrubber portion of the system could not be calculated because the chromium emissions generated by the electroplating setup were not measured. Ambient chromium concentrations near the tank were also not measured.

4 Pilot Demonstration of VVST Using Downflow Tubes (Prototype 1)

Due to promising initial tests, the Castle Hone and Lap system (CH system) was constructed and installed by Benet Laboratory in their Vessel Plating Facility at Watervliet Arsenal in Watervliet, NY. Testing was performed on 13, 14, 18, 19, and 20 March 1996, by MSE Technology Applications, Inc. (MSE-TA), assisted by Benet Laboratory. The brief 5-day testing period did not allow for many adjustments in the testing procedure and equipment, or the CH system itself. For this reason, some of the collected data provided are only estimates of the actual performance.

The objectives of the demonstration were to evaluate the overall impact of the CH system on ambient chromium concentrations in the chromium-plating area, and to determine the ability of the CH system to reduce chromium emissions. The device was shown to control emissions below the strict California standard and to meet OSHA's standard for ambient concentrations. The system's effectiveness is mostly attributed to a significant reduction in created emissions by pulling the gas bubbles from the plating tank before they burst.

Pilot Experiments

Experimental Setup

The pilot demonstration was performed in a modified chromic acid holding tank. The tank is 48.5 in. wide x 73 in. long x 90 in. deep and was filled with 1230 gal of chromic acid. The cathode/anode rack was manufactured with a CPVC backing with a copper bus overlay for the anodes. Two cathodes manufactured of 2-in. diameter standard steel pipe were placed in the center of the rack. These cathodes were replaced with spares during the demonstration if the voltage across the plating system became too high to maintain a constant current.

Twenty anodes manufactured from ½-in. lead wire were placed through holes in the copper bus. Anodes were also replaced as needed during the demonstration whenever high voltages become a problem. Both the cathodes and anodes

extended 80 in. below the top of the tank and approximately 70 in. into the chromic acid solution.

The anodes and cathodes were fed by a 9-volt rectifier with 1500-amp of current. A recirculation pump provided the driving force for maintaining the liquid vortex within the tank; the pump was operated at 40 to 60 gal per minute. The airspace between the surface of the chromic acid and the tank lid (freeboard) was maintained at approximately 10 in.

The CH system was designed to fit the above plating configuration for the demonstration. The venturi/vortex portion consists of six, 0.75-in. diameter vortex drains, each with a 2-ft serpentine section, evenly spaced along the length of the tank. These drains each feed into 1-in. pipes that all feed into the separation chamber. The separation chamber consists of two, horizontal, 2-in. pipes spanning the length of the tank near the bottom below the venturi/vortex scrubbers. All pipes are constructed of CPVC and were placed inside the tank. The drains are positioned just under the plating solution. During the demonstration, it was found that the device is very sensitive to the liquid level. The addition of 5 L of liquid to the 5200 L tank caused a rise in liquid level of only 2 mm; yet this small change greatly affected the flow rates through the CH system. During sampling, the tank liquid level (which gradually decreased with time) was continually monitored and adjusted. Figure 2 shows a diagram of the venturi/vortex scrubbers.

Figure 3 shows a schematic of the entire CH system. The liquid recycle line exits the tank, goes through the pump, and re-enters that tank on the opposite side of the scrubbers through a perforated piping network. This provides an even distribution of the liquid recycle and sufficient solution mixing. The filter-condenser unit is constructed of two, vertical, 2-in. CPVC pipes. Due to the experimental nature of the system, exhaust from this unit was vented into the existing scrubber unit, except when samples were collected by flowing the entire stream into the impingers.

Sampling Methodology

Ambient Air Samples. Ambient samples were collected using the National Institute of Occupational Safety and Health (NIOSH) Method 7024. A Gilian portable sampler was used to draw air through a 0.8 micron filter at a rate of approximately 3 L per minute. The filter was analyzed by C-Tek Laboratories of Dallas, TX (American Industrial Association Hygiene Laboratory Accreditation No. 57) for chromium content. Six samples were taken over two, 1-hour periods,

concurrent with gas stream sampling experiments. The samples were taken 5 ft from the chromium electroplating tank and approximately 5 ft above the floor level. This location represents a worst case worker exposure scenario.

Gas Stream Samples. Figure 3 shows gas stream samples taken at the four different locations (sampling point numbers 3, 4, 5, and 6). Point number three (P3) is located just above the plating tank in the base of the existing stack. The sampling port was a 1-in. pipe attached perpendicular to the stack. Samples were taken here with the existing ventilation system running and the CH system not running. These samples were used to determine the amount of chromium emissions generated under normal operating conditions. However, the sampling at this point was not performed isokinetically, with standard traversing, nor satisfying flow disturbance criteria. This sampling technique makes the accuracy of the data collected at this point questionable. These samples probably represent a concentration lower than that actually exiting the stack because the largest particulates that contribute significantly to the mass would probably not be able to make the 90-degree turn into the sampling port. Three tests were performed at this sample site, two with the lid present (P3-1 and P3-2) and a third with the lid absent (P3-3).

Sample point number four (P4) is located in the airspace between the lid and the plating solution near the venturi/vortex drains. The objective of these samples is to quantify the chromium concentration entering the CH system. Three tests were performed using this sample site as well, two with the lid (P4-1 and P4-2) and a third without the lid (P4-3).

Sample P5-1 was taken at sample point number five (P5), which is positioned just downstream of the CH system's filter-condenser unit. The data from this test was used to determine the amount of chromium emitted from the CH system in its normal operating configuration (lid present).

Sample point six (P6) is located just upstream of the filter-condenser unit, but downstream from the venturi/vortex portion of the CH system. Data from this location was used to determine the comparative effectiveness of the two portions of the CH system (sample P6-1, lid present).
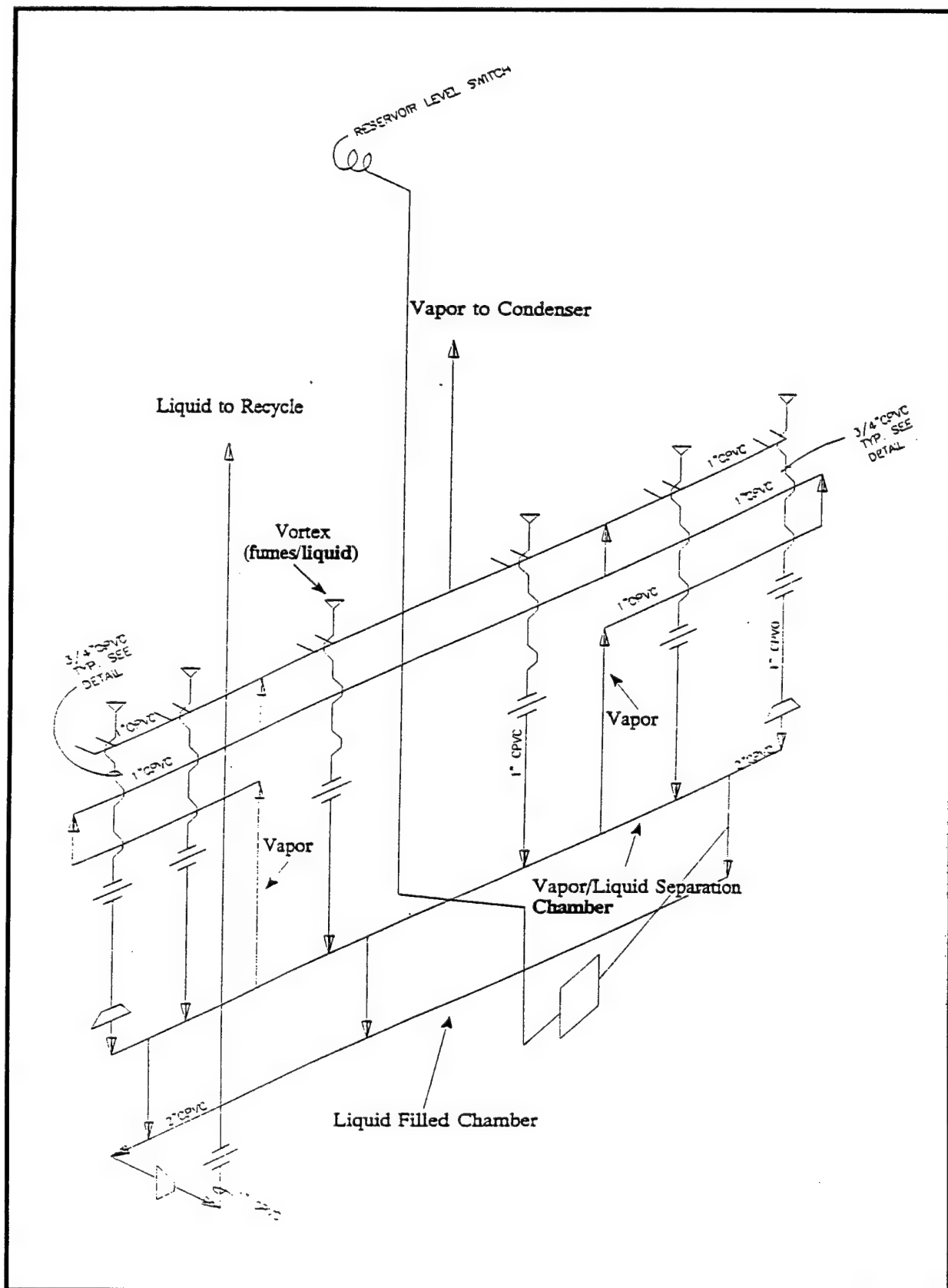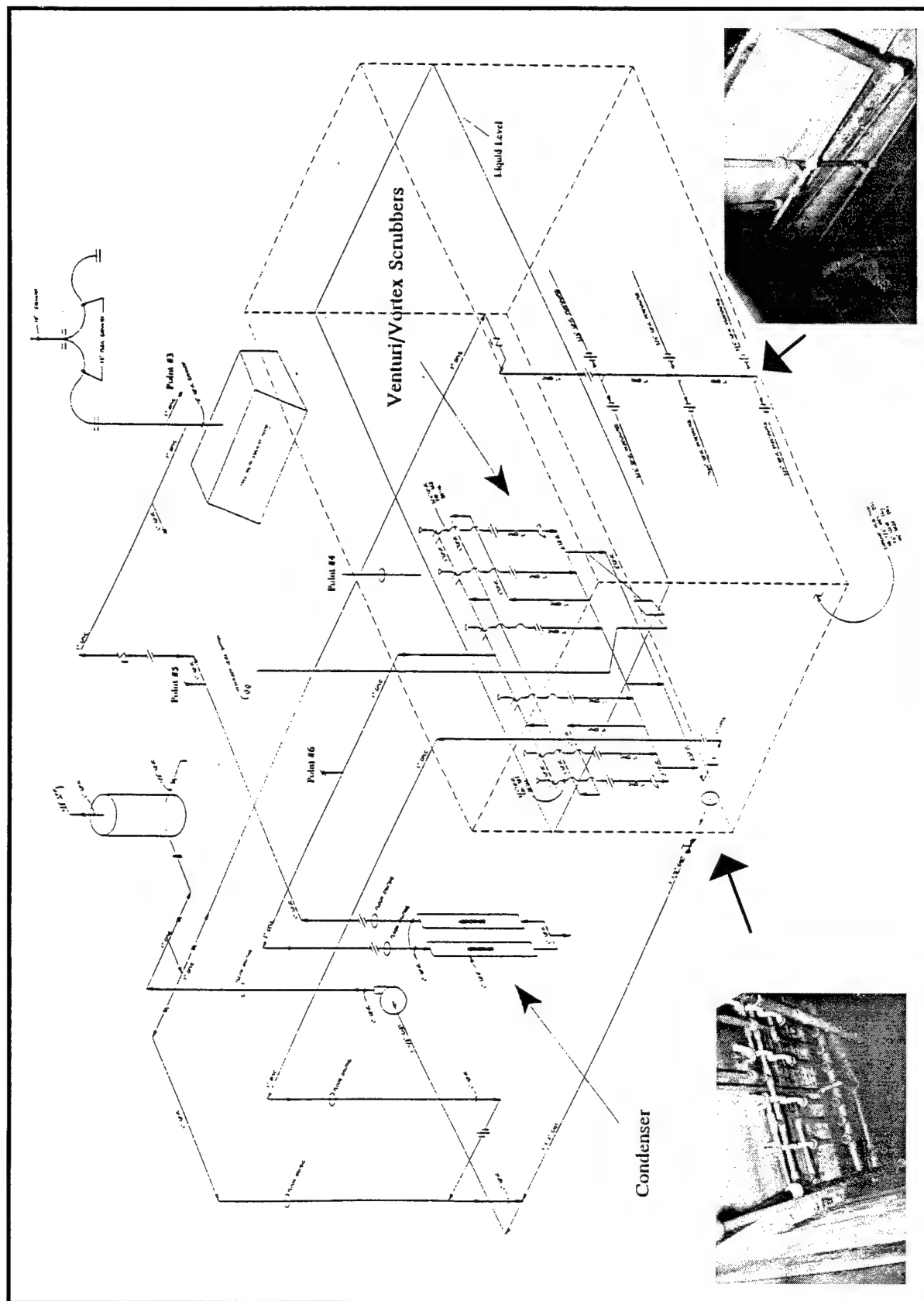
Figure 2. Venturi/vortex scrubbers as configured for pilot demonstration.

Figure 3. Complete Castle Hone system configuration for pilot demonstration.

All gas stream samples were collected using EPA Method 6A with considerable modifications. The sampling train consisted of the following components in downstream order: two glass (Greenburg-Smith) impingers containing 0.1N NaOH; an empty glass impinger; a glass impinger with silica gel desiccant; and a NuTech Model 2010 control box, including a sample pump and a calibrated dry gas meter. Samples were analyzed by CTM Laboratories of Latham, NY using method 3010 of SW-846, EPA Method 200.7.

At P5 and P6, the entire gas stream was allowed to flow passively into the impinger train once an initial representative flow rate was established. At both of these sample points, the pressure from the CH system was low, and maintenance of the plating tank chromium level within a very narrow range was required to maintain a steady flow rate. At P6, sample flow rates averaged around 0.3 standard cubic feet per minute (scfm), with each sample collected over a 2-hour period. At point 5, the pressure from the CH system was so low that a flow rate (to the dry gas meter) of only 0.075 scfm could be maintained; because of this, a single sample of 7 hours duration was performed to ensure the collection of a measurable amount of chromium.

At P3 and P4, it was necessary to draw a sample using a vacuum pump. The flow rate was set to approximately that observed at P6 during the P6 series tests. All P3 and P4 samples were collected over two, 1-hour periods.

Condensate Samples. Samples of the condensate from the condenser-filter unit were taken over approximately eight, 1-hour periods in a 5-gal sealed container. The samples were analyzed for chromium content and volume also by CTM Laboratories. These measurements were taken to check mass balance calculations at the filter-condenser unit.

Experimental Results

Ambient Chromium Concentrations

Ambient chromium sampling was conducted during gas stream test series P3, P4, and P5 to compare ambient concentrations during normal plating operations (with the existing scrubber) versus CH System operation, and to determine the effect of the tank lid position. Table 1 lists the results.

Table 1. Summary of analytical results for ambient air samples.

Sample Number	Corresponding[1] Gas Stream Sample	Sample Date	Sample Time	Plating Cover	Scrubber	Sample Volume (1)	Chromium Conc. (mg/m³)
3A-1	P3-1	03/13/96	10:39 a.m.	Closed	On	343.2	0.00262
3A-2	P3-3	03/20/96	9:40 a.m.	Open	On	343.2	0.000583
4A-1	P4-1	03/14/96	9:32 a.m.	Closed	Off	343.2	0.00294
4A-2	P4-2	03/14/96	12:18 p.m.	Closed	Off	343.2	0.00315
4A-3	P4-3	03/20/96	12:55 p.m.	Open	Off	343.2	0.0241
5A-1	P5-1	01/19/96	11:00 a.m.	Closed	Off	343.2	0.0160
[1] Denotes that the ambient air sample in question was performed concurrently with the indicated gas stream sample.							

During the P3 test series, where the system was running with the existing scrubber and not the CH system, one ambient test was conducted with the plating tank lid open (P3-1) giving a result of 0.003 mg/m³. The result for the sample taken with experiment P3-3 with the lid closed is 0.001 mg/m³. Compared to the OSHA standard of 0.05 mg/m³, these results indicate that the in-stack blower draws chromium emissions from the plating tank sufficiently well that the presence of the lid is not important (CFR 29:1910).

With the P4 test series (conducted during operation of the CH System), two tests were conducted with the tank lid closed and one with the lid open. With the tank lid closed, the ambient concentration was measured as 0.003 mg/m³. This is the same as observed with the in-stack blower alone. However, the ambient concentration increased to 0.024 mg/m³ when the lid was open. These results indicate that the CH System, with the lid absent, allows some chromium fumes to escape into the ambient air instead of being processed by the CH System. Note, however, that these samples were collected during the P4 sampling event, when a gas stream sample was being drawn at a flow rate approximately equaling the flow rate through the CH system. Therefore, the total amount of gas drawn from above the plating solution was twice the amount drawn by the CH system itself. Nevertheless, it appears the system keeps the ambient concentration below the OSHA level. Considering the large increase in ambient concentrations with the lid removed, it is recommended that this unit be operated with the lid closed. Recently published discussion of a more stringent OSHA standard supports this idea (Altmayer 1996).

An ambient test was conducted concurrently with gas stream test P5-1, and these results were also elevated at 0.016 mg/m³. During this test, the entire CH System gas stream was sampled passively. The flow rate into the impingers was about 80 percent lower than for the passive tests conducted at P6 (upstream from the filter-condenser assembly). This indicates a reduction of the system flow pressure across the filter-condenser assembly, and suggests that the sampling train itself may have introduced some back pressure to the system. Due to the reduced the gas intake into the CH system, emissions may have been

able to escape through holes in the tank lid, leading to elevated ambient concentrations.

Gas Stream Concentrations

Table 2 lists a summary of gas stream sample results, and also shows mass flow rates and the corresponding ambient and condensate sample results. The observed gas stream chromium concentrations are consistent with previous expectations. The highest concentrations were observed during the tests conducted at the airspace below the lid of the chromium plating tank (P4 series). The scrubber system was not operating, and the gas being sampled had not yet been processed by any portion of the CH System. Concentrations averaged around 100 mg/m^3 for tests P4-1 and P4-2 (lid closed). However, the measured concentration was only 15.586 mg/m^3 for test P4-3 with the lid open. The open lid may account for this difference. This is supported by the corresponding higher ambient concentrations.

The next highest concentrations were observed at P6 (just downstream of the venturi/vortex scrubber portion of the CH System). Results for test P6-1 are considered questionable because a significant leak in the impinger train was discovered at the conclusion of the test. This problem was corrected for tests P6-2 and P6-3. Tests P6-2 and P6-3 give an average result of 4 mg/m^3, or approximately 4 percent of those observed in the P4 series tests with the tank lid closed. This indicates significant reduction of chromium concentrations by the venturi/vortex scrubber portion of the CH System.

Further reduction in the chromium concentration was observed with test P5-1 (downstream of the filter-condenser unit). The measured concentration is 0.177 mg/m^3. This is less than 5 percent of the concentration observed on the upstream side, and less than 0.1 percent of the concentration in the gas stream entering the CH System.

The tests conducted under normal plating conditions with the in-house blower running (P3 series) yielded an average chromium concentration of 0.08 mg/m^3. This concentration is less than observed with the CH system due to the larger gas flow rate.

Table 2. Summary of chromium sampling results.

Gas Stream Test No.	Sample Date	Gas Volume Sampled (sq ft)	Water Fraction	Amount of Chromium captured (mg)	Mean Tank Amperage (amp)	Total System Flow (scfm)	Mean Chromium Liquid Flow (gal/min)	Gas Stream Chromium Conc. (mg/m³)	Gas Stream Chromium Conc. (mg/amp-hr)	Ambient Chromium Conc. (mg/m³)	Mass of Chromium In Condensate (mg)
P3-1	03/13/96	40.186	0.026	0.084	1490	401.00	N/A	0.074	0.034	0.002820	
P3-2	03/20/96	39.562	0.028	0.306	1438	401.00	N/A	0.273	0.129	N/A	
P3-3	03/20/96	39.128	0.025	0.161	1512	401.00	N/A	0.145	0.065	0.000583	
P4-1	03/14/96	40.257	0.123	141.300	1505	0.075	57.1	123.951	0.010	0.002940	875[1]
P4-2	03/14/96	40.531	0.133	97.650	1500	0.075	52.9	85.083	0.007	0.003150	
P4-3	03/20/96	38.746	0.070	17.100	1342	0.075	51.6	15.586	0.001	0.024100	132.3[2]
P5-1	03/19/96	31.435	0.033	0.158	1492	0.075	51.2	0.177	<0.001	0.016000	86700[3]
P6-1	03/18/96	28.135	0.251	13.475	1514	0.25	54.9	16.914	0.005	N/A	53750[4]
P6-2	03/18/96	34.398	0.161	4.560	1504	0.31	55.6	4.609	0.002	N/A	
P6-3	03/18/96	36.916	0.137	3.634	1516	0.33	54.3	3.476	0.001	N/A	

[1] Collected during tests P4-1 and P4-2
[2] Collected during test P4-3
[3] Collected during test P5-1
[4] Collected during tests P6-1, P6-2, and P6-3

Condensate Samples

The rate of chromium capture in the condensate jug is several orders of magnitude higher than would be expected from the entrance and exit concentrations. It is suspected that some of the liquid plating solution spilled over into the vapor section of the system and flowed into the condensate jug. Because of this problem, these data are not considered. Fortunately, the mass balance check is not critical for evaluation of the CH System's efficiency, as gas stream concentrations are the most significant. Any liquid exiting the system via the condensate reservoir would be pumped back into the plating tank in an industrial application. Therefore, this portion of mass represents no environmental or fugitive loss of chromium from the system.

Evaluation of CH System Effectiveness

Chromium Emissions Generation

The total chromium emissions generated by the experimental chromium electroplating setup are calculated in two ways:

1. By taking the average concentration found in the gas stream during the P3 test series, and multiplying this value by the total flow rate past the sample point. This resulted in a total chromium emission rate of 0.076 mg/amp-hr, or 1.862 mg/minute. This value is meant to represent the amount of emissions generated by the plating configuration without the CH system running.

2. By taking the average concentration found in the airspace below the plating tank lid during the P4 test series (with the tank lid closed), and multiplying by the average flow rate through the CH System measured at P5 (this measurement was taken just prior to the P4 test series sampling at P4) by two (CH system and the sample train). This method yielded a total chromium emission rate of 0.018 mg/amp-hr, or 0.450 mg/minute. This result represents the amount of chromium emissions generated with the CH system running. These results are considered reliable, but there is some uncertainty regarding the actual flow rate through the system during this test; it is suspected that the sampling train itself restricted flow. Also, this calculation is valid only if a steady-state concentration had been achieved by the chromium plating process, which was difficult to determine.

As discussed above, the concentration data obtained during the P3 test series are not representative of the actual concentration flowing up the existing stack. Additionally, the total flow rate in the stack was not measured during sampling; it was assumed to be identical to the rate measured during compliance sampling several years previously. The USEPA has found that large variations in the generation of chromium emissions have been reported, and it has been difficult to correlate these with respect to plating variables (Deitz et al. undated). It seems that a correlation in plating usage, in terms of ampere-hours, has provided the best estimation, which is 10 mg chromium/amp-hr (USEPA 1993). It is reasonable to assume that the generation with this experimental setup was at least 1.0 mg/amp-hr, since the USEPA found no sites producing less than this value.

The difference between the two above calculations for the emissions generation is an important result. It shows that the CH system prevents the creation of a large portion of particulate emissions by collecting the unpopped gas bubbles. Based on the two calculated values, a 76 percent reduction is realized. By substituting the conservative estimate based on the data of the USEPA for the emissions generated without the CH system, it is estimated that 98 percent of the potential emitted chromium is never produced.

Chromium Emissions Reduction

The chromium removal efficiencies are calculated for the two portions of the CH system, and as a whole. For these calculations, it is assumed that the total flow rate through the CH System is represented by the flow measured at P5 (0.075 cu ft/minute, or 0.0021 m^3/minute), as this is the outlet of the system. This assumption may be questionable, however, since the gas sampling train itself may have decreased the flow at P5.

The efficiency of the venturi/vortex scrubbers portion of the system is calculated on the basis of the chromium mass entering the scrubber versus the amount exiting it, using sampling results from test series P4 and P6. The average mass rate of chromium entering the CH system is calculated as 0.4390 mg-Cr/min (0.0088 mg/amp-hr), and leaving the venturi/vortex scrubbers as 0.0085 mg-Cr/min (0.0014 mg/amp-hr). This indicates the removal of 0.4305 mg-Cr/min and a collection efficiency of 98.1 percent across the venturi/vortex scrubbers.

The effectiveness of the filter-condenser portion of the CH system is determined by calculating the mass of chromium removed from the vapor stream across the filter-condenser unit, based on sampling results from test series P5 and P6. The

average chromium mass rate entering the filter-condenser unit is calculated as 0.0085 mg-Cr/min (0.0014 mg/amp-hr), and exiting the unit as 0.00037 mg-Cr/min (0.00002 mg/amp-hr). This gives a collection efficiency of 95.6 percent through the filter-condenser unit.

The overall efficiency of the CH System for removing chromium from the gas stream was calculated based on sampling results from test series P4 and P5. The average chromium mass rate entering the CH system is calculated as 0.4390 mg-Cr/min (0.0088 mg/amp-hr), and leaving the system as 0.00037 mg-Cr/min (0.00002 mg/amp-hr). This gives an overall collection efficiency of 99.9 percent.

These efficiencies indicate that the CH system achieved a significant reduction in chromium emissions. Exit chromium mass emissions meet the California standard of 0.006 mg-Cr/amp-hr, even with just the venturi/vortex portion of the system. However, the concentration measurements do not meet the USEPA National Emission Standard for Hazardous Air Pollutants (NESHAP) standard of 0.015 mg/dscm (Federal Register vol 60). The USEPA based its standard on available control technologies that rely on a large volumetric air flow rate for ventilation and dilution. Note that USEPA approval for an alternate technology exception would be necessary for this technology to be implemented in actual production settings.

Conclusions of Demonstration

The CH system as modified for this pilot demonstration is effective in reducing the chromium concentration of plating tank emissions. The most significant reduction in emissions is a result of emission prevention. At least 76 percent (and up to 98 percent) of the emissions were prevented by capturing the unpopped gas bubbles. Of the remaining emissions, the reduction across the CH system is 99.9 percent, and a reduction of 98.1 percent was accomplished by the venturi/vortex scrubber portion alone. Concentration data collected upstream from the filter-condenser assembly show that the CH System's venturi/vortex scrubber portion alone achieved compliance with California standards. Measured Chromium emission rates at this location were in all cases 0.005 mg/amp-hr or less, compared against the standard of 0.006 mg/amp-hr. The CH system as a whole reduced the emissions to 0.00002 mg/amp-hr, more than two orders of magnitude less than the standard. However, due to the low gas flow rate, the concentration exiting the device does not meet the USEPA NESHAP limit. An exception would be needed for compliance.

There are several issues regarding the operation of the CH system during this study:

- The system is very sensitive to the liquid level in the plating tank.

- The system, as set up, was able to keep the ambient concentrations below the OSHA standard of 0.05 mg/m^3. However, two factors greatly increased the ambient concentration: the removal of the lid and the downstream restrictions that reduced the gas flow rate through the system. While the filter-condenser assembly provided additional reductions in chromium emissions, it decreased the total flow through the CH System by 80 percent. The sampling train is also suspected of reducing the flow rate. Ambient samples taken when the sampling train was not connected to the CH system yielded lower concentrations. Another consideration is that OSHA may decrease their standard by one to two orders of magnitude in the near future (Altmeyer 1996). These factors all suggest that an increase in the gas flow rate is desirable.

- The lid could pose an operational problem for facilities that have frequent part removal/placement.

- There were many difficulties in testing this device, which contributed to the unreliability of some data. The most significant was that sampling the emissions from the 1-in. diameter stack required sampling the entire exhaust stream. This gave accurate chromium mass collection, but restricted the gas flow giving poor gas flow rate measurements. This uncertainty in the gas flow rate affected emission concentration calculations through the system.

Despite these issues and the uncertainties with some of the experimental results, the simplicity and relatively low cost of the system warrants further development. If increased gas flows through the system can be obtained and a solution to the liquid level sensitivity can be developed, this method may provide a cost-effective means for the plating industry to achieve emission compliance.

5   VVST Using Siphon Tubes (Prototype 2)

The promising results from the pilot demonstration prompted improvements in the VVST. Robert Castle made several design modifications and was contracted to construct and test the new design at USACERL. This new design is an attempt to correct the primary problem of the original device, its strong dependency on plating solution level.

Prototype 2 Description

The main differences between prototype 1 and prototype 2 are that the liquid drains are replaced with siphon tubes and the gas/liquid separator uses centrifugal ejectors to help separate the gases. Figure 4 shows an overall picture of the device. Air is injected into the liquid flow through small holes in the siphon tubes placed just above the plating solution. This design also requires a loose fitting tank lid.
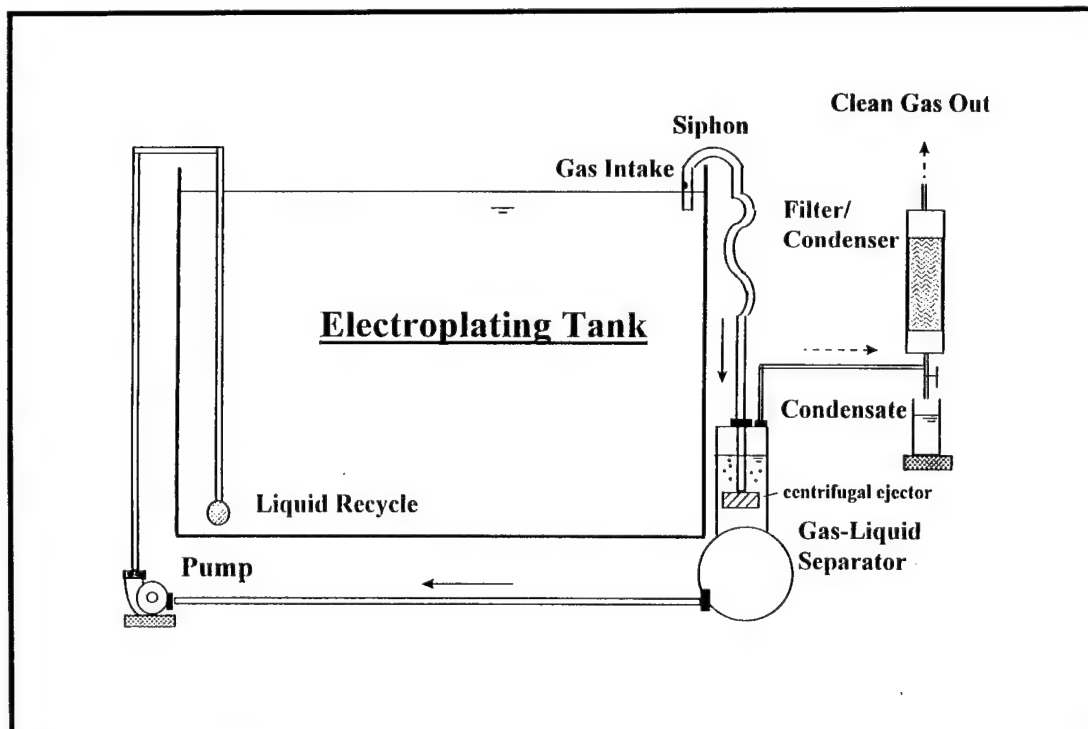
Figure 4. VVST design No. 2.

Each tube has its own ejector that sprays the liquid/gas mixture in a circular motion within a pipe. The separated gas exits the top of the separation chamber through a pipe that joins the other separation chambers. This pipe leads to the filter condensor unit, which is identical to the unit used with prototype 1. The liquid collects at the bottom of the horizontal pipe that joins the individual separation chambers. A pump recirculates the liquid back into the tank while gas exits the top of the separation chambers and flows through the filters/condensors. This unit is designed to reside outside the plating tank.

Experimental Setup

Robert Castle of Castle Honing and Lap constructed a complete prototype 2 at USACERL during August and September 1996. Due to the extremely hazardous nature of chromic acid, testing was performed using an air/water system only. The objectives of the experimentation were to observe the functionality of this new device, to see if the flaws of the previous design had been corrected, and to provide an opportunity to improve the design by adjusting an actual working model.

The device was installed on a 40-in. wide x 46-in. long x 40-in. deep polyethylene container (Bonar Plastics). The tank was filled to approximately 6 in. below the top with water. The device includes four siphon tubes, each with its own separation chamber. One of the siphon tubes is constructed of clear tubing so that the gas/liquid mixture can be observed as it descends. All other piping is constructed of PVC. Figure 5 shows the installed system. Figure 6 shows the siphon intakes (small air holes and pierced intake white PVC pipe sections just above the liquid level). The water was pumped by a 1 hp centrifugal pump and measured with a standard water meter totalizer. Air flow rate was measured using a Gilibrator Primary Flow Calibrator (Gilian Instruments Group).

The experimentation was primarily exploratory, involving much observation and system adjustment, but few data recordings. The operation of the system was videotaped and photographed. Data recorded were gas/liquid ratios with various arrangements. System adjustments included varying the size and number of air intake holes in the siphon tubes, varying the liquid level in the tank, and changing the number of siphon tubes used.
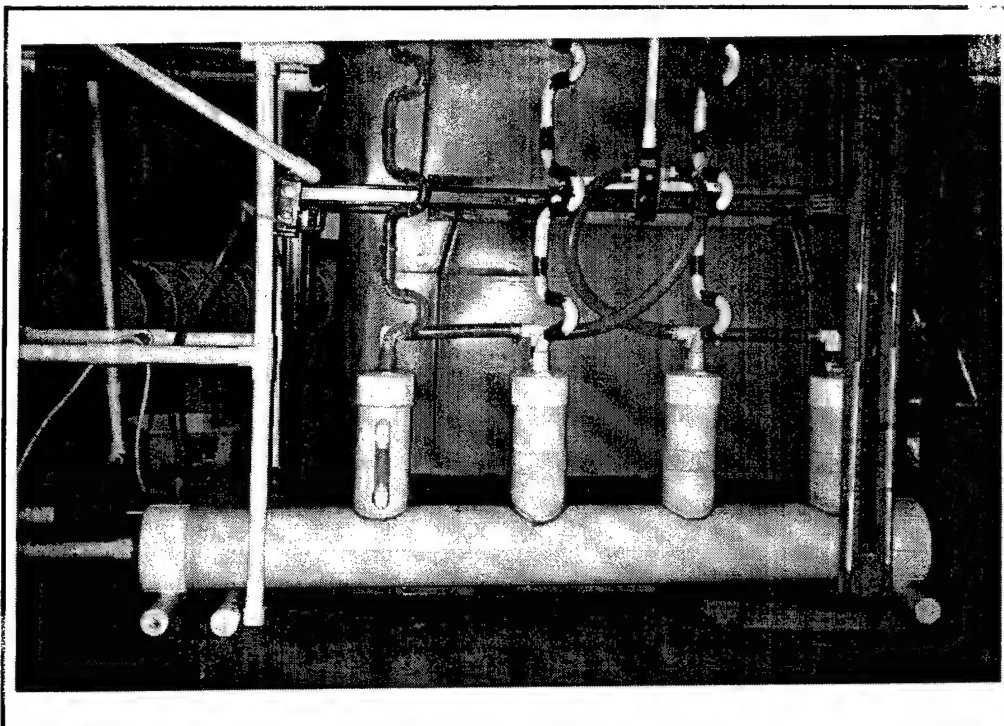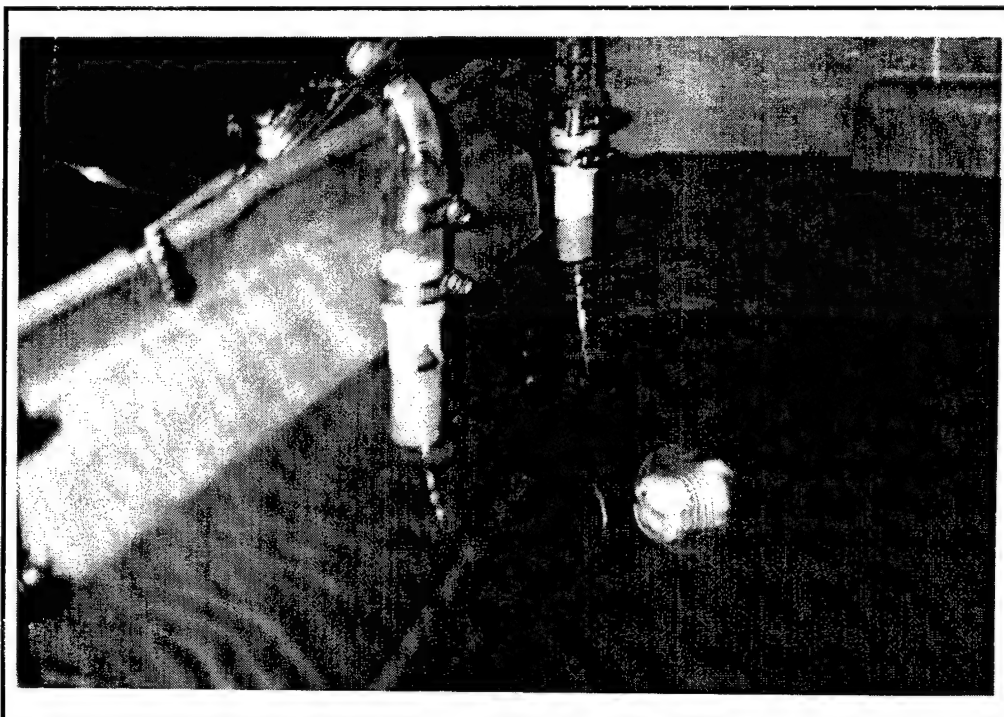
Figure 5. Installed system.

Figure 6. Siphon intakes.

Results and Discussion

Photographs taken of the clear tubing show that gas bubbles gently mix as they proceed downstream. The bubbles tend to flow in the regions of lowest speed around the bends of the tube. This is because the centrifugal forces on the more dense liquid push the liquid to the outside of the bend and the less dense gas to the inside (Figure 7). It is questionable whether, in an actual electroplating application, this would provide adequate mixing to scrub the particulates inside the captured air and to coalesce the gas bubbles captured in the liquid line.
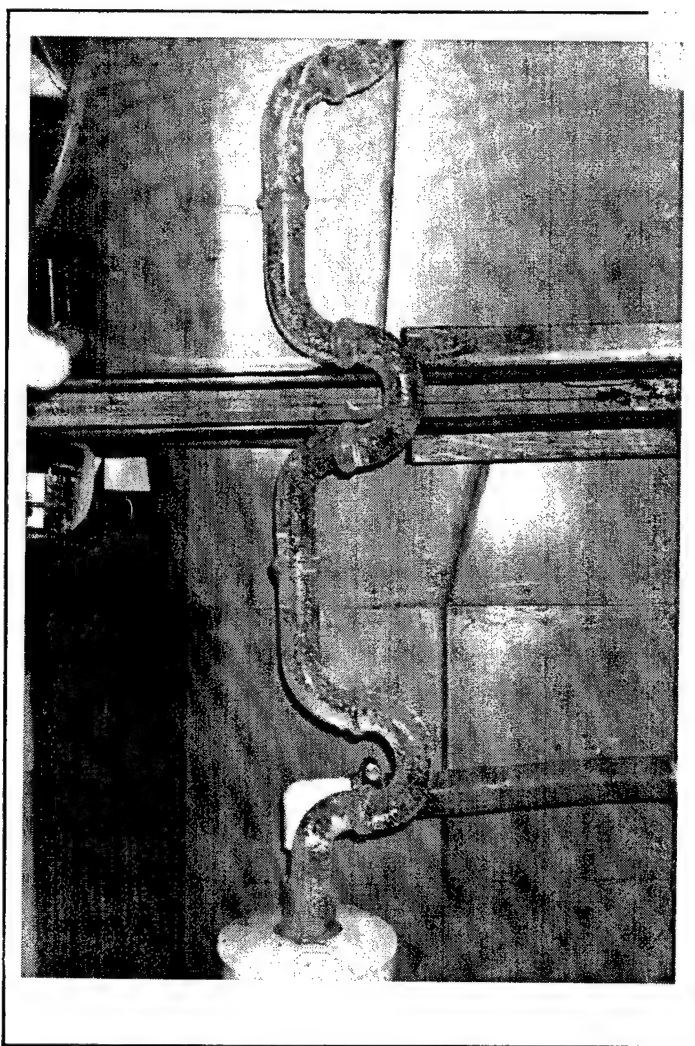

Figure 7. Centrifugal forces push the liquid to the outside of the bend.

Experiments with two tubes resulted in an average water flow rate of 17.4 gal per minute (gpm) and an average gas flow rate of 17.0 L/min, giving an average gas /liquid volume flow ratio of 0.258. Experiments with three tubes resulted in an average water flow rate of 11.2 gpm and an average gas flow rate of 11.3 L per minute (L/min), giving an average gas/liquid volume flow ratio of 0.267. It was found that the device could not maintain a siphon when all four siphon tubes were used. These gas/liquid ratios are more than one order of magnitude larger than that observed during the pilot demonstration of the original design.

The primary result of the experiments was the finding that there is an ideal operational condition for the system, depending on how it is arranged. The device is very sensitive to changes in liquid height, number of siphon tubes, number and size of air holes, and gas back pressure in the air exit line. It is difficult to adjust the system to operate in a stable condition. It is common for the system to eventually lose the siphon and stop operating. When stable operation was achieved, the device was kept at the gas/liquid flow ratio of approximately 0.26 where stable operation is defined as maintaining a constant level of liquid in the separation chamber and working siphons for at least 10 minutes.

The testing of this second prototype has led to the conclusion that the design inherently possessed two competing actions. It was desired for the gas flow rate to be increased for better control of released emissions and better mixing in the downflow tubes. It was also desired that the device achieve a state of stable reliable operation. However, when a siphon was used to draw the liquid and gas from the tank, it as found that maximizing the gas intake increasingly jeopardized the ability for the device to maintain the siphon. Lowering the level of the plating solution in the tank also increased the chances for the siphon to break. For this device to be useful in industry, it must be reliable (i.e., allow a minimal chance of disruption in the operation). To correct this problem, a major design change would be necessary.

6 True Venturi Implementation (Prototype 3)

As discussed in the previous chapter, Prototype 2 possessed a major flaw that unfortunately makes it unsuitable for implementation into industry: the chance for breaking the siphon and stopping the liquid flow. Immediately after the testing of Prototype 2, USACERL personnel attempted to completely redesign the device while maintaining the basic principle by which the device had shown promise (using bubble capture and separation as the primary method). This effort resulted in the invention of Prototype 3.

Prototype 3 Description

Prototype 3 of the Venturi/Vortex Scrubber Technology controls the toxic air emissions by preventing their production just as the previous versions do (by removing generated gas bubbles from the tank before they burst). However, in this prototype, the liquid drawn from near the plating solution surface (by siphon) is pumped through a venturi throat where air from above the tank is injected into the liquid stream to coalesce the gas bubbles and scrub the particulates automatically from the injected air. Pulling air from above the tank serves as a secondary control to help capture fugitive emissions to be recycled. The liquid/gas mixture passes through a hydrocyclonic separator positioned mostly inside the plating tank. The plating solution exits the separator at the bottom and returns to the tank. The gas leaves the top of the separator and flows into a filter/condenser unit. This unit contains a composite mesh pad to remove particulates in the gas stream. The lower temperature of the unit promotes condensation that further aids in the removal of the contaminant by increasing the particle sizes and providing wetted surfaces for the particles to adhere. Clean gas leaves the plating facility through a small stack. Figure 8 shows a basic diagram of the system.

As with the previous designs, this device may require the use of a loose lid to prevent fugitive emissions from entering the worker breather zone. This requirement will be tested during the upcoming ESTCP Demonstration.
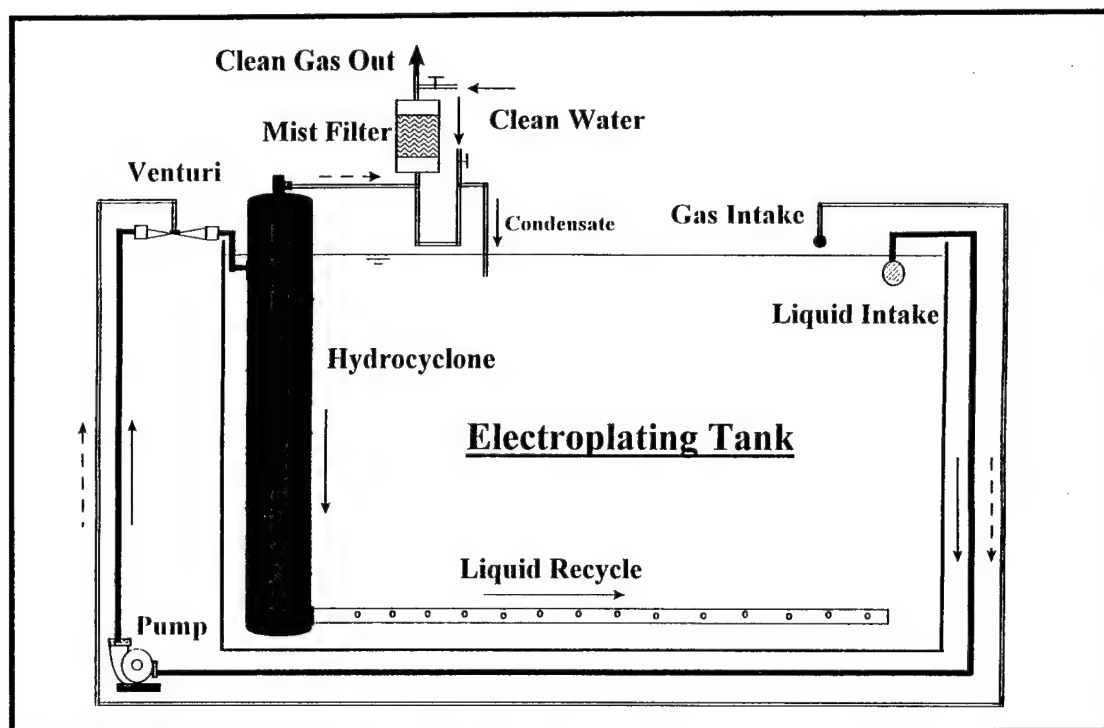
Figure 8. VVST design No. 3.

All piping on this device must be compatible with chromic acid. The majority of the construction is of CPVC (chlorinated polyvinyl chloride) with some PVDF (polyvinylidene fluoride) fittings, including the gas injector (venturi).

It is estimated that between 76 and 98 percent of the emissions were controlled just by capturing bubbles with the original version of this technology (Hay et al. 1997). Many improvements and major conceptual changes have since been made to enhance this performance as well as other aspects of the device such as increased gas flow, better separation, and superior reliability.

Experimental Setup

Experimental work was done using an air/water system. This prototype was set up in the same tank used in the experimentation with prototype 2. The water is pulled off the tank through 2-in. diameter PVC (polyvinyl chloride) horizontal distribution pipe placed approximately 6 in. below the surface of water. The liquid is pumped through 1.5-in. diameter PVC piping by a 2 hp centrifugal pump. The liquid is forced through a Mazzei model 2081 PVDF (polyvinylidene fluoride) gas injector. With this setup, the maximum liquid flow rate is 50 gal per minute at a maximum pressure of 30 pounds per square inch (psi) upstream

of the venturi. The vacuum created due to the pressure drop across the venturi throat pulls in an approximate maximum of seven cu ft of air per minute.

The air/water mixture is injected into a custom made separator made of clear Plexiglas for visualization. The body of the unit is 8-in. diameter pipe approximately 5 ft tall. In an actual electroplating application, the separator would be placed inside the tank, but, for experimental purposes, this prototype was positioned just outside with the liquid return exiting the bottom of the separator and then going back over the edge of the tank. The separator uses centrifugal forces to bring the lower density gas bubbles to the center of the unit and the liquid to the walls as the mixture flows in a vortex manner around the separator. This technique is common with hydrocyclones. Plastic guides direct the liquid flow down to the bottom of the separator and a stationary tube with slots in the center allows gas to rise. The development of the separator was based on trial and error modifications to the basic hydrocyclone design. According to Bradley (1965):

> Data on which to base the design of a gas separator or with which to predict the separational aspects is not known. One reason is that bubble size particularly in the presence of shear is an unknown. Another reason is that the separation is simply performed and it is technique which is important.

Figure 9 shows the experimental separator.

The separated gas exits the top of the separator though a clear plastic tubing connected to a gas flow meter. A Gilibrator Primary Flow Calibrator was used to measure gas flows below 30 L/min and an air rotameter (Blue White Industries) for gas flow rates above. The pressure entering and exiting the venturi in the liquid line were monitored by pressure gauges. The exit gas pressure and air intake vacuum were measured by manometer.

Figures 10 and 11 show the experimental setup. The experimental system does not include a filter/condenser unit. An adjustable restricted valve was placed at the end of the gas line to mimic a pressure that would be introduced by the filter/condenser. The black section of piping just to the right of the separator in the pipe leading into the side of the separator is the gas injector. The large piping exiting the separator bottom is the liquid return line. The air intake into the venturi is the clear tubing attached to the top of the gas injector.
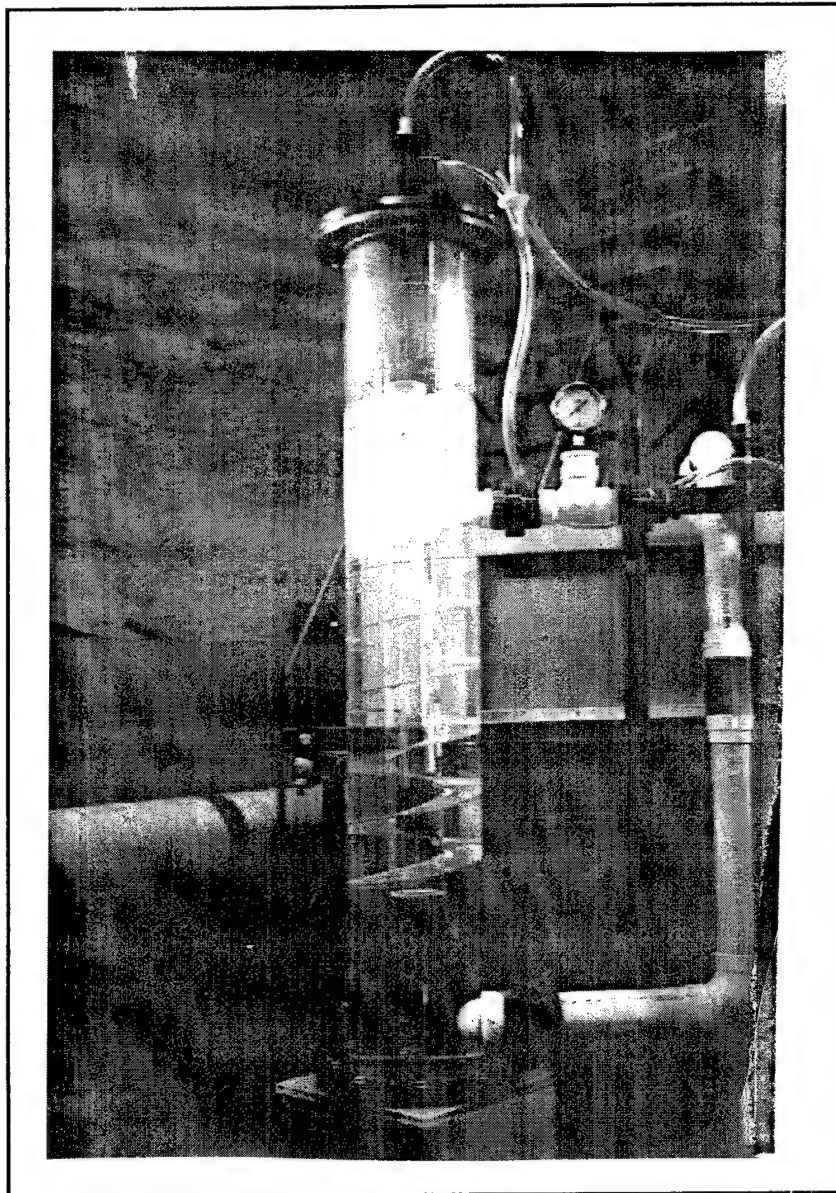
Figure 9. Experimental separator.

The primary goal of the experimentation was to determine the air/water ratio under different liquid flow rates, the ability of the separator to coalesce and eliminate gas bubbles from the liquid, and best operational conditions and limitations of the device. Several injectors with different sized throats were tested. Development of the third prototype was similar to that of the second prototype; experimentation was comprised primarily of product development work with few data recordings, and much observation and adjustment of the system.
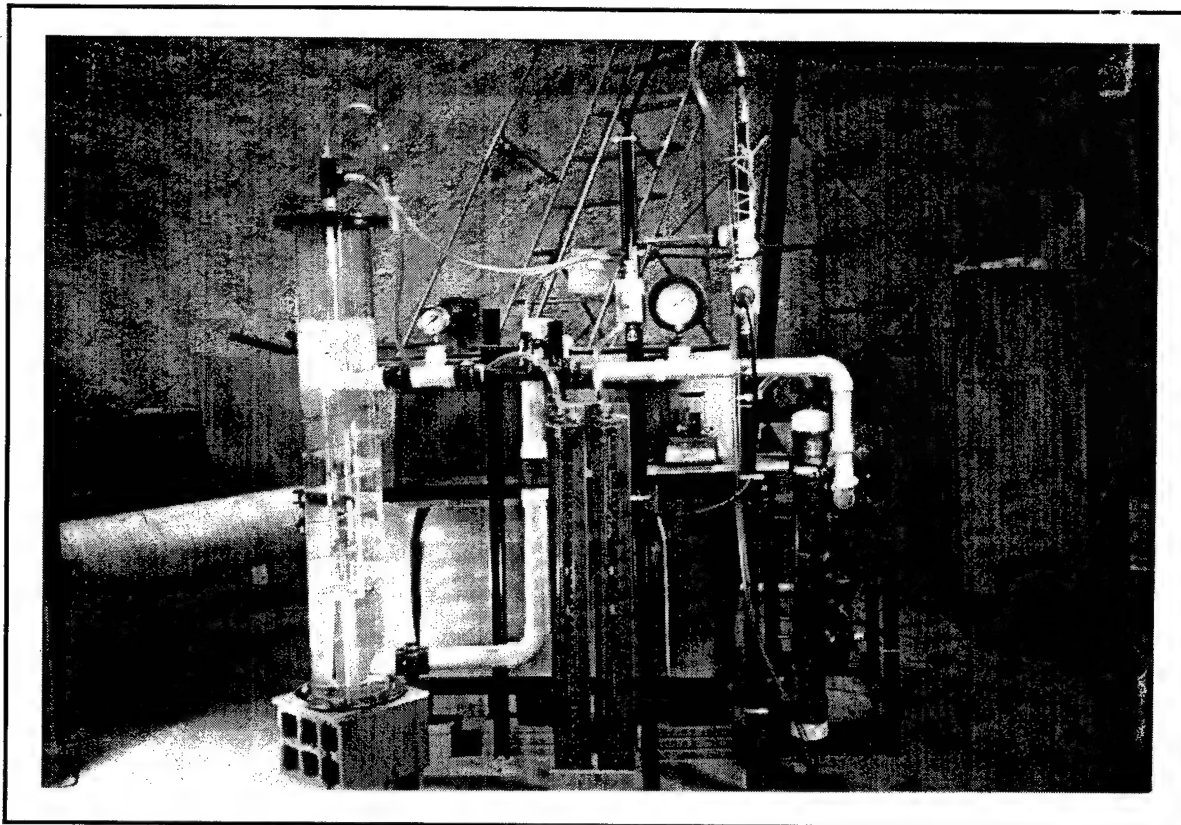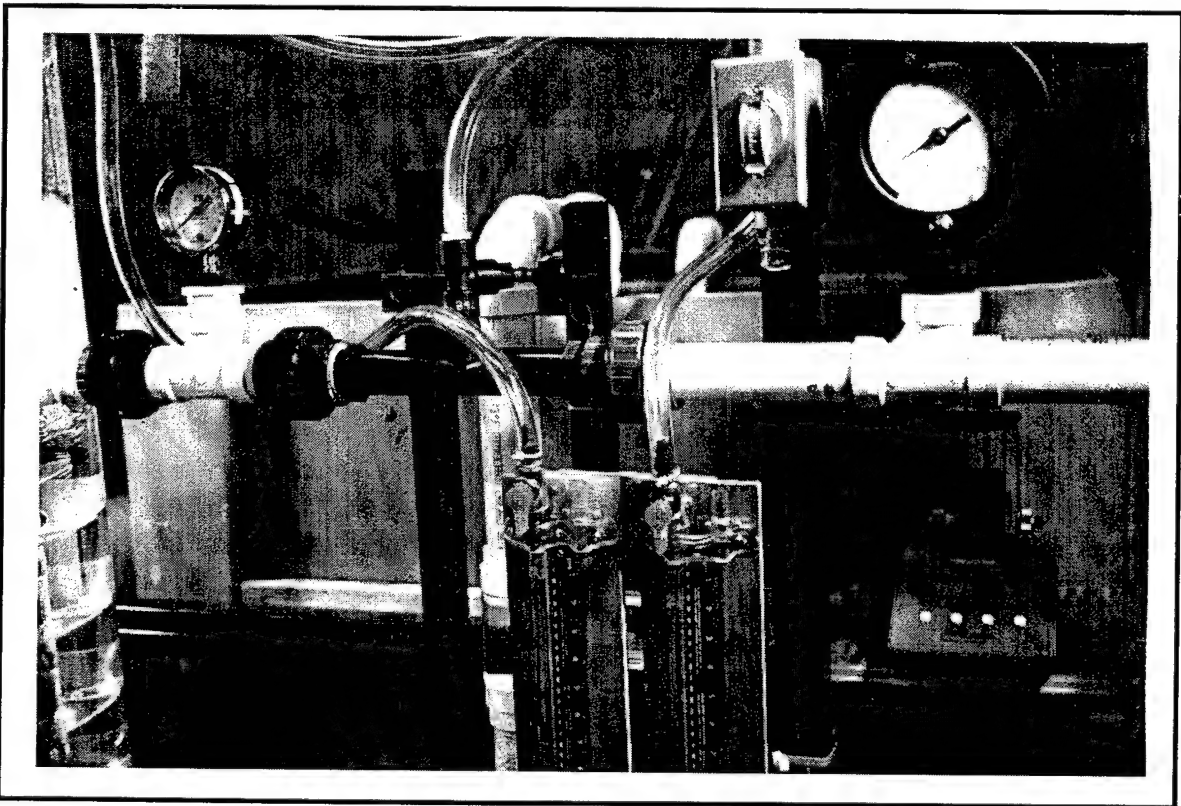
Figure 10. Prototype 3 experimental setup—overview.

Figure 11. Prototype 3 experimental setup—focus on gas injector.

Results and Discussion

Two experiments were performed using a Mazzei model 1584 gas injector. Data from these experiments are shown in Figures 12, 13, and 14. The amount of restriction in the gas line exiting the separator was changed between the first and second tests. This is evident by the increased gas back pressures shown in Figures 12 and 13. This had little effect on the ability of the separator, but a large effect on the height of the water in the separator. In the first experiment, the level was between 20 and 30 cm above the gas/liquid mixture inlet, but only between 5.5 and 1.3 cm in reference to the inlet for the second experiment. Figure 14 shows that the liquid to gas flow ratio remained fairly constant between the tests. It is suspected that the slightly lower values of the black circles are due to a leak found in the gas measurement system found after the experiment.

Very good gas/liquid separation was observed for gas flows up to about 40 L per minute (L/min). Above this level, an appreciable amount of small bubbles begin to flow out the bottom of the separator and back into the tank.
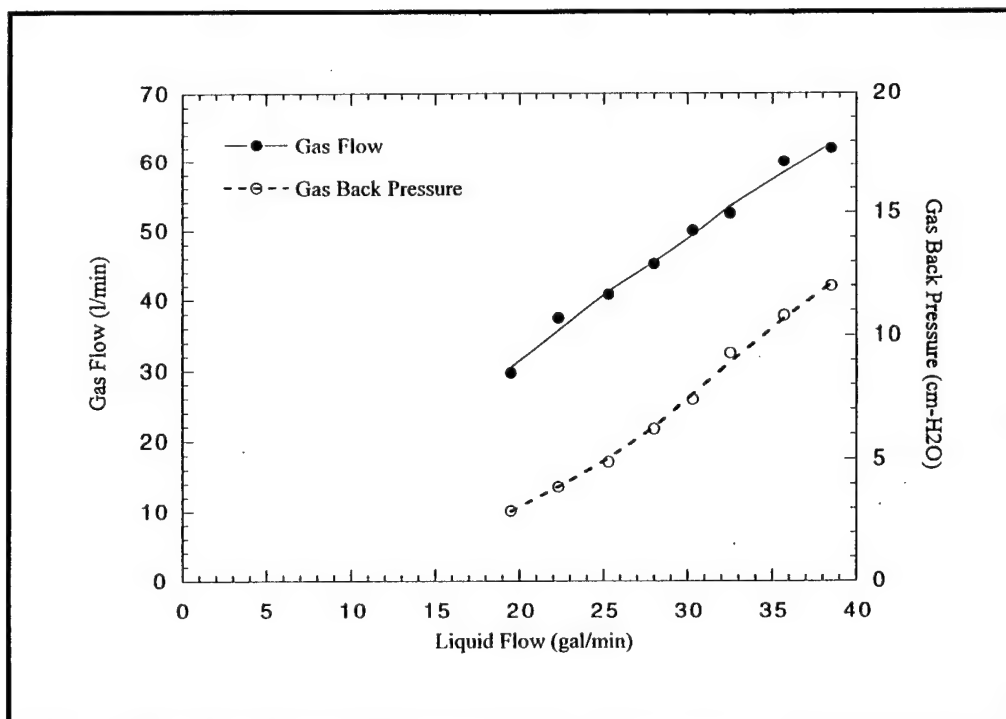

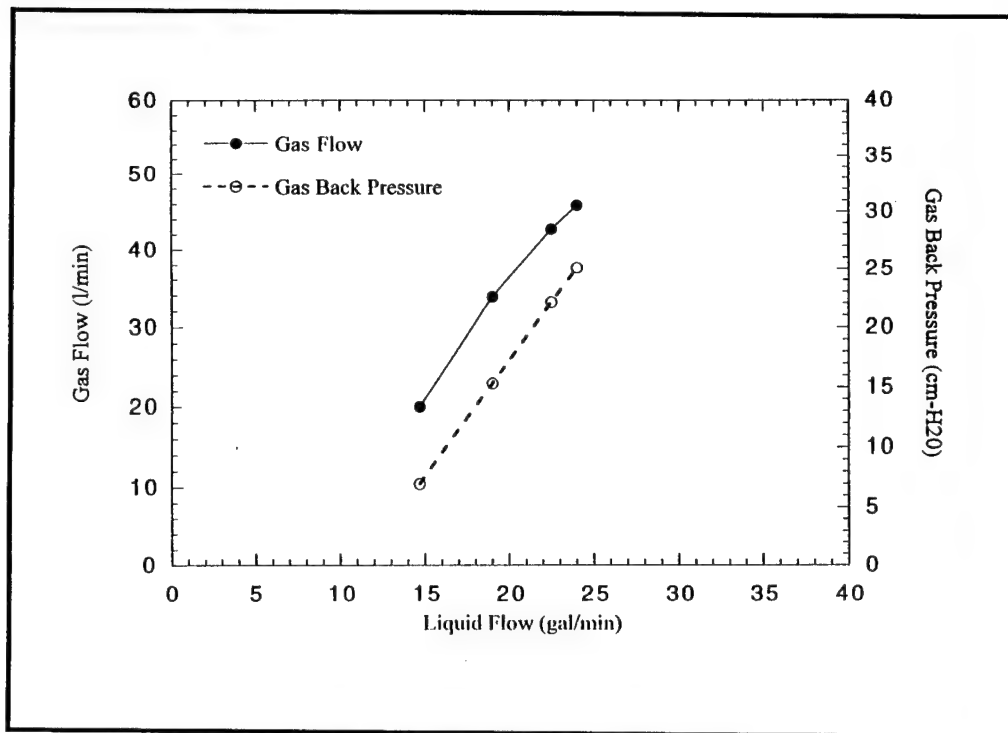**Figure 12. Gas back pressure, experiment #1, model 1584.**

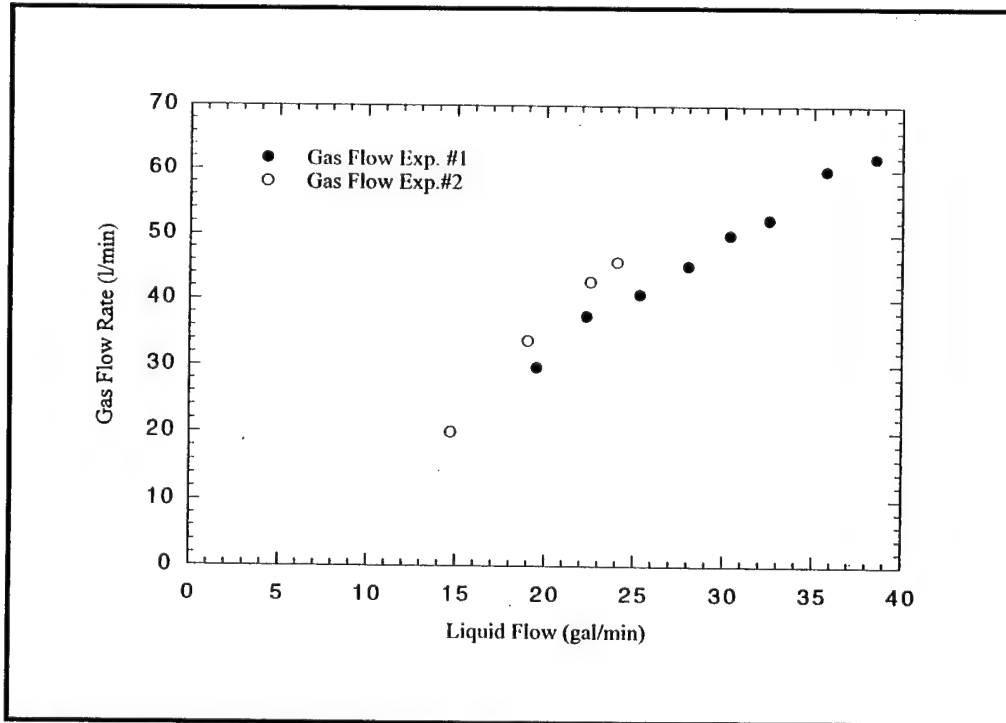**Figure 13. Gas back pressure, experiment #2, model 1584.**

Figure 14. Gas/liquid ratios, model 1584.

A test was also performed using Mazzei model 1583 gas injector. The throat of this venturi is smaller than that of model 1584 resulting in a much higher gas/liquid ratio. Again, the separator performed well up to 40 L/min of gas flow, but only 20 gal per minute of liquid was needed to achieve this gas flow. With this venturi, a more violent mixing occurred generating a greater number of smaller size bubbles. With increased liquid flow rate, this presents a more difficult separation problem.

Mazzei model 2081 venturi was also tested. The fittings on this venturi are 2 in. (others are 1.5 in.) so reducers were placed in line to accommodate the larger pipe size. The gas/liquid ratio of this venturi is similar to model 1583, but the larger size keeps the bubble fines to a minimum. Figure 15 gives data from this test. During these tests, the back pressure in the gas exit line was regulated between 22 and 33 cm of water. At the highest liquid flow, the water level in the separator reached to top of the separator, a condition not desired. This result suggests that the prototype separator is undersized for this venturi. This venturi is a good size for actual application to standard sized plating tanks and the separator could be enlarged to accommodate the extra flow. For all of the readings in Figure 14, separation was very good for large bubbles, but a few small bubbles did manage to escape. It was observed that the bubble sizes were larger than the other model venturis so that separation was more efficient.

The measurements taken for the gas/liquid flow ratios were found to be consistent with the provided manufacturer specifications of the tested venturis.[*] The specifications take into account the water flow rate and downstream back pressure for each venturi. During the test of model 2081, a maximum volume gas/liquid ratio of 0.95 was achieved. This value is higher than the values achieved with prototypes one and two (0.04 and 0.26 respectively). With a larger pump, an even larger ratio could be reached through this venturi. However, qualitative observations at 5 cu ft per minute gas flow indicated that it may still be difficult to keep chromium concentrations above a plating tank at levels consistent with conventional devices, especially without using a lid. This will be tested in the upcoming ESTCP demonstration.

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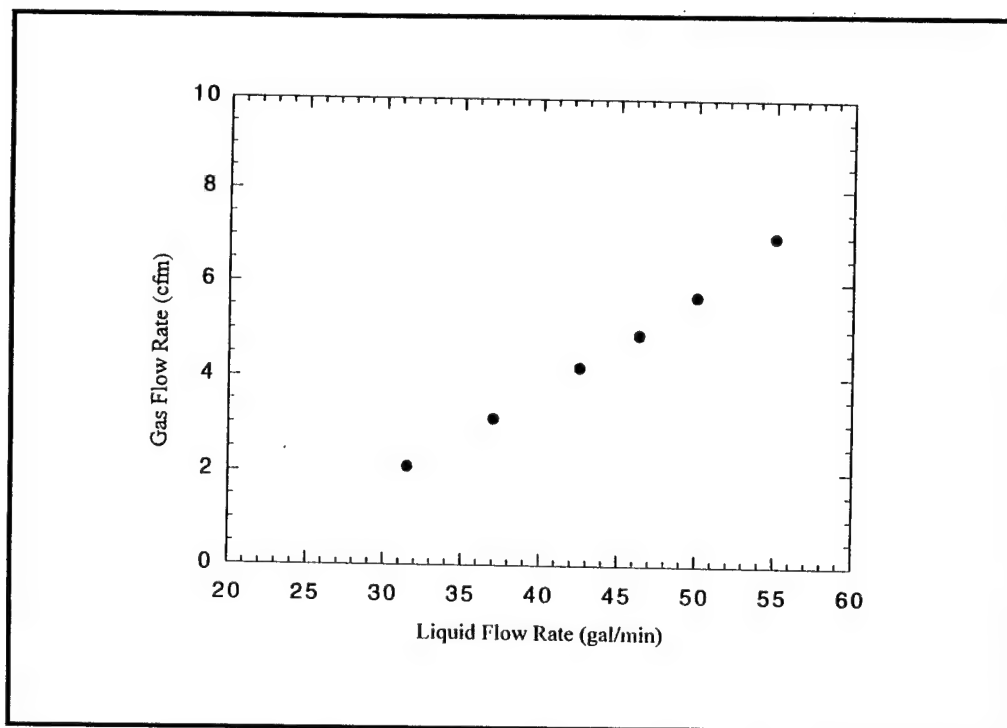
Figure 15. Gas/liquid ratios, experiment #3, model 2081.

Advantages and Limitations

This technology has a number of advantages over conventional end-of-pipe control technologies:

- It lowers capital and maintenance costs.

- It eliminates scrubber wastewater. (No wastewater is generated with this system.)

- It minimizes space requirements. (The system requires no extensive ventilation system.)

- It replaces conventional air circulation for the plating tank. (Air circulation promotes emission generation.)

- It uses less energy. The liquid pump uses less energy than a large blower, and this device does not vent a large amount of climatized air to the outside as do conventional systems.

- It controls vapor and heat loss from the tank (if a lid is used.)

- It lowers maintenance costs.

- It allows chromium recovery. (Some conventional devices do not recycle collected chromium.)

Disadvantages associated with this technology include:

- The system may possibly require a lid. Operators may not accept this additional step in their electroplating procedures.

- Operators must be aware of air withdrawal location without lid. A flexible air withdrawal will need appropriate positioning during plating.

- The system uses some space in plating tank.

- The technology is not yet USEPA accepted.

- Each electroplating tank may require a unique design.

- This technology's ventilation system is not compatible with automated plating operations.

- This system has not yet been tested in an actual chromium-electroplating tank.

Design Considerations

One favorable characteristic of this technology is that the design can be modified to accommodate a wide variety of electroplating configurations. The drawback of this, of course, is that, in a multiple-tank facility, each tank may require its own design. It is because of this that a specific design for the technology cannot be given, but some guidelines for determining the most appropriate design for a given case can be specified.

All piping that comes into contact with the chromic acid solution should be Schedule 80 CPVC. Some piping can be Schedule 40 CPVC such as the liquid return distribution pipe and the stack exiting the filter unit.

Pump and Venturi

Deciding on the appropriate liquid flow rate is the main design criteria. During the pilot demonstration, a 50 gal per minute flow rate was used for a tank with 1500 gal of plating solution and a cross section area of 24 sq ft (6 x 4 ft). The data gathered from this test indicated that this liquid flow rate was sufficient to collect over 98 percent of the unpopped bubbles. This value is the only valuable information on the pump sizing thus far. It seems that the cross sectional area of the tank would be the most important characteristic since the idea is to pull off the plating solution near the plating solution surface. Using this criteria, a flow rate can be determined by:

$$U_L = (50gal \, / \, min) * SA \, / \, 24 sq \, ft \qquad \qquad \textbf{Eq 1}$$

where SA is the surface area and U_L is the liquid flow rate. This number should be treated as a minimum design flow rate.

Once the liquid flow rate is determined, a desired gas flow rate can be estimated by expecting to achieve at least a 0.5 gas/liquid volume flow ratio. Mazzei specifications give venturi characteristics at given liquid flow rates and inlet pressures. The experiments discussed in this report show that this chart can be trusted for determining the appropriate venturi if selecting this manufacturer. To achieve a given gas flow rate, a specific inlet pressure must be achieved. The pump characteristics should be presented to prospective pump manufacturer as a certain liquid flow rate at a given pressure.

One factor that must be considered is that the solution is concentration chromic acid at a temperature near 130 °F (for 30 percent chromic acid, the specific gravity is 1.2). This will change the pumping characteristics slightly. It is also important to realize that the pumps and venturis only come in specific sizes so choices may be limited by availability and/or the design may be dictated by the most convenient components. The pump and venturi must be constructed of materials that are compatible with chromic acid solution. The design should at least ensure the minimum flow rate specified above.

Liquid Intake

The liquid intake needs to be designed to pull generated bubbles across the tank width. The wider the tank, the more difficult this requirement becomes. The simplest design leads to a horizontal pipe that extends the length of the tank and is positioned along one side of the electroplating tank. The pipe should be placed at a minimum of 6 in. below the surface to avoid creating a vortex and pulling in air at the solution surface. The pipe contains multiple holes facing directly towards the plating area that are sized and spaced according to the dimensions of the system installed. Angled CPVC baffles can be placed at the top of the sides (near the surface of the solution) to help divert liquid rising on the side of the tank to flow across the top of the tank towards the liquid intake. The only difficulty with this design is contending with obstacles along the tank wall. Tanks with sidewall obstructions and/or widths of greater than 4 ft may require modifications to this design.

Gas/Liquid Separator

The typical design should position the separator resting on the bottom of the plating tank with the gas/liquid mixture entrance located just below the plating solution surface. With this design, the height would be determined by the height of the tank. With a deep tank (deeper than 10 ft), the separator could be mounted on the tank wall so that it does not need to extend to the bottom.

It is important to provide adequate head space in the separator for adjustments in the back pressure of the gas line. The liquid level in the separator is a function of back pressure of gases and pressure required to return the liquid to the plating tank. A low gas pressure allows the liquid in the separator to rise to the top while a high gas pressure can cause stratified flow to develop in the spiral flow guide vanes of the separator. (Both conditions are undesirable.) If a significant liquid flow resistance exists in the separator, the same effect of a low gas pressure will develop. For successful operation, an equilibrium must exist that keeps the liquid level at a position just above the gas/liquid mixture entrance. To achieve this, minimal restrictions should be allowed in the liquid flow so that the gas back pressure becomes the limiting design criteria. Ideally, minimal restrictions in the outlets of both phases will allow equilibrium to be near ambient pressure.

Sufficient back pressure is needed to drive the gases passing through the filter/condenser media (composite mesh pad). The pressure drop through a wet commercial mesh pad may be obtained from the manufacturer. Given the gas back pressure and the resistances of fittings, flow guide, and distribution pipe, an average liquid level in the separator may be estimated using Bernouli's equation. An allowance of about 30 in. of water pressure for the gas back pressure is reasonable.

The spiral flow guide helps to prevent short flow and to maintain a well defined tangential flow in the separator. The design of this guide influences the pressure drop of the liquid in the separator. Reduction in spacing between two spiral vanes increases the pressure drop, which can increase the separator efficiency. However, this will also result in an increase in liquid height in the separator. A balance of good efficiency and low pressure drop will result in a typical vane separation of about 4 in.

It is difficult to eliminate all restrictions in the liquid exiting the separator, especially due to the spiral guide. Extra space above the gas/liquid entrance (more than 2 ft) should be present to accommodate some rise in liquid head.

The liquid should exit out the bottom of the separator through a liquid return distribution pipe that imposes very little or no resistance to the flow.

The separator efficiency is a function of separator diameter, feed flow rate (tangential velocity), liquid residence time, pressure drop, and properties of gases and liquids. In general, the efficiency decreases with an increase in separator diameter and increases with an increase in feed flow rate, pressure drop, and residence time (Bradley 1965). The separator diameter, D1, has to be small enough to achieve a desired separator efficiency and large enough to keep the separator height reasonable for a given liquid residence time. The average liquid residence time in the separator, t, is approximated by:

$$t = \frac{p\,(D_1^2 - D_2^2)\,H}{4U_L}$$

Eq 2

where:

    D_2 = external diameter of the internal tube

    H = the liquid level

    U_L = the liquid flow rate given by Equation 1.

With the design to be installed during the upcoming ESTCP demonstration, D_1 = 10 in., D_2 = 3 in., U_L = 50 gal/min, and H = 84 in., giving a residence time of 31 seconds. This is about twice the residence time of the prototype used for experimentation.

Liquid Return

The separated liquid exits the bottom of the cyclone separator and should be diverted in a manner to establish a rotational pattern in the tank. The flow pattern should help bring the liquid near the surface towards the liquid intake. A simple design is to have the liquid distributed out a large pipe extended across the bottom of the tank and directed towards the opposite side that the liquid intake resides. Again, angled CPVC baffles along the tank sides at the solution surface would help to direct the flow towards the liquid intake.

Lid and Air Intake

The lid consists of several sections. First, it is recommended that excess plating surface be covered with fastened lids (these lids should be removable for tank repairs). The working area should be covered with loose, easily moved lid

sections that either lift or slide back and forth. These lids should all be constructed of PVC sheets or any other insulating material that is compatible with concentrated chromic acid.

Air Treatment

It is important to minimize the pressure drop in the gas line. Use oversized piping between the separator outlet and the filter/condenser unit (2-in. CPVC piping is adequate). The filter unit is approximately 8 in. in diameter (CPVC pipe shell) and tall enough to house up to two, 6-in. thick composite mesh pads. The top needs to be removable so the pads can be periodically cleaned and/or replaced. A deionized water line should be plumbed into the top of the unit for periodic rinsing. The stack exiting the unit should also consist of oversized piping and extend outside the plating facility and above the roof line. A condensate return line should allow condensate and rinsewater to flow back into the plating tank. The pipe should contain a U-tube section similar to conventional drain pipes to prevent gas from exiting. The condensate line can also serve the purpose of an emergency spillover line in the remote chance the separator overflows with liquid.

Economic Analysis

The cost estimate presented here for an actual implementation of design number three is an approximate based on expected components for a 2000-gal tank with dimensions of 11 ft long x 3 ft wide x 8 ft deep. The exact sizing of the pump for such a tank is currently unknown, but is being explored in an ongoing related demonstration project. Another unknown is the impact of this device on wastewater treatment. Capital costs are estimated at $15,000 plus an additional $5,000 for installation. Annual costs including energy, labor, and chromic acid recovery are estimated at $5,000.

All cost figures will be analyzed in much greater detail and accuracy during the demonstration/validation phase of this technology. When comparing the VVST to conventional technologies, the following costs will be considered: design, equipment, materials, installation, and permitting actions. Annualized costs will include energy usage, operating labor, maintenance, hazardous disposal, water usage, wastewater treatment, chromic acid recovery, monitoring, and indirect costs such as overhead.

7 Hazards Analysis

The primary safety concern is exposure to chromic acid as a concentrate in the plating solution and as airborne liquid particulates generated during the electroplating process. Hexavalent chromium is a known carcinogen and chromic acid solutions in high concentrations are highly corrosive. In general, these risks are common to chromium electroplating operations. The standard health and safety rules of an installation with a chromium electroplating operation using this technology should be followed to ensure that personnel are at the least risk possible. This device differs enough from conventional air pollution control equipment that some additional safety issues need to be addressed.

Additional Safety Issues

The largest health and safety concern for using this technology will be the worker breather zone hexavalent chromium concentration. The VVST is designed to prevent this concentration from approaching or exceeding the OSHA standard, but it is possible, particularly during operations not using a tank lid, that this standard may not be met.

A large amount of CPVC plumbing is attached to the Venturi/Vortex unit. All pipes, with exception of air treatment pipes, should be located in, above, or near the chromium tank so that any spills from leaks that develop will stay in the tank or fall into the containment pit associated with the tank.

There should be safety switches attached to the centrifugal pump for automatic shutdown in the case of improper operation. The conditions that should trigger the switches are if the liquid level reaches the top of the separator and if the pressure drop across the filters/condensers exceeds a predetermined level.

Safety Plan

The following modified version of the Safety Plan has been incorporated into the Demonstration Plan for the continuing ESTCP Demonstration/Validation project at MCLB Albany, GA.

B.1 General Safety Guidelines

The following procedures should be followed to ensure the greatest safety:

- Wear safety goggles.

- Be aware of the location of the eyewash and shower in the work area.

- Clean up acid spills immediately if outside of catch basin.

B.2 Maintenance Safety Guidelines

- Wear protective gloves and clothing when working with Venturi/Vortex unit.

- Make sure the power is off before working with the unit.

- Ensure that tank current is not applied before turning unit off.

- Before removing the pump for servicing, ensure that the valves on both sides of the pump are closed.

- The mesh pads in the filter/condenser units will contain chromic acid. Be sure to wear complete protective gear when cleaning or replacing these pads.

B.3 Emergency Shutdown

In the event that ambient chromium concentrations become noticeably high (either visibly or through odor), the following procedures should be followed:

- Remove personnel from the plating area.

- Put on respirator equipped with toxic particulate and acid gas protection.

- Disconnect the applied current to stop the electroplating process.

- Turn on room ventilation system. If a pre-existing air treatment system for the tank is still present and operational, turn that system on.

8 Summary

Chromium electroplating is used extensively throughout the Department of Defense for plating a variety of military parts. Chromium is a difficult surface coating to substitute due to its combination of qualities. However, due to the carcinogenic properties of hexavalent chromium, air emissions from the chromium electroplating process are highly regulated at all government levels. Conventional technologies for controlling these emissions are expensive and cause additional water pollution problems. This has provided an opportunity for development of alternate technologies to reduce costs and pollution.

The Venturi/Vortex Scrubber Technology is a newly developed technology for controlling hexavalent chromium air emissions from DOD chromium electroplating operations. This technology has gone through three developmental prototypes to reach its final design. The first prototype was demonstrated at an Army facility and was shown to meet applicable emission standards, but with unstable operation. Prototype two provided some improvements in the system, but failed to correct the primary problem of instability. The final prototype involved a complete redesign of the system to develop a stable device. This design also significantly improved the volume gas/liquid ratio (from 0.04 and 0.26 of the first two prototypes to 0.95).

Design number three uses a gas/liquid injector to mix the plating solution and air from above the tank. The gas/liquid mixture is separated using a custom-made hydrocyclone. The gas is treated with a composite meshpad before exiting outside the plating facility. The plating solution is redistributed into the plating tank. Each tank will require its own unique design. The primary design considerations are the dimensions of the tank, the amount of plating, and obstacles in the tank. This device will be tested at the upcoming ESTCP demonstration at MCLB Albany, GA, and Hill AFB, UT.

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Abbreviations

CPVC	Chlorinated polyvinyl chloride
DOD	Department of Defense
dscm	dry standard cubic meter
ESTCP	Environmental Security Technology Certification Program
MACT	Maximum Achievable Control Technology
NESHAP	National Emission Standard for Hazardous Air Pollutants
OSHA	Occupational Safety and Health Administration
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
USEPA	U.S. Environmental Protection Agency
VVST	Venturi/Vortex Scrubber Technology

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